

PATENT SPECIFICATION

NO DRAWINGS

856.792



Date of Application and filing Complete Specification: April 24, 1959.

No. 14146/59.

Application made In United States of America on May 7, 1958.

Complete Specification Published: Dec. 21, 1960.

Index at acceptance:—Class 98(2), D(8:12G).

International Classification:—G03c.

COMPLETE SPECIFICATION

Receiving Sheet for use in Photographic Silver Transfer Process

5 We, GENERAL ANILINE & FILM CORPORATION, a corporation of the State of Delaware, United States of America, located at 230 Park Avenue, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the reproduction of photographic images wherein a silver halide image is transferred imagewise to a receiving sheet for development and particularly to the constitution of such a receiving sheet.

15 The process whereby the residual silver halide in a negative silver image is utilized to form a positive image upon a transfer or receiving material is known as the diffusion-transfer process. According to this process, the material to be copied is used to form an image on a light sensitive silver halide emulsion which, for the sake of simplicity, can be designated as the negative material. In those areas of the negative material struck by light, a negative latent image is formed while those areas not struck by light contain a positive image of unexposed silver halide. The exposed negative material is then treated with a developer composition containing a silver halide solvent and a silver halide developing agent after which the wet, exposed negative material is contacted with a receiving material comprising a piece of paper or foil containing a fogging agent and silver halide solvents.

35 The developer composition causes the development of the negative latent image in the negative paper; the silver halide solvents in said developer composition react with the unexposed silver halide to form soluble silver complexes which are transferred by diffusion to the receiving material and are there acted upon by the fogging agent therein, whereupon said silver halide complexes are transformed to metallic silver or silver compounds of high optical density.

[Price 3s. 6d.]

Although the diffusion-transfer process has found rather extensive application in the commercial market, it suffers from certain drawbacks and disadvantages, especially as regards the nature of the receiving material employed. Many commercial receiving materials, after processing, have a decided hazy or spotted appearance, a characteristic which is particularly objectionable when transparent receiving materials are used. Another drawback is a marked yellow discolouration of the background areas on ageing. In addition, these transfer foils have, after processing, a very tacky surface, such defect being particularly noticeable when the final copy is handled with damp fingers or under conditions of high humidity.

The receiving materials made in accordance with the above-mentioned diffusion transfer process may be prepared by coating gelatin from a water solution onto a base. This use of water, as the solvent, leads to problems such as long drying periods at fairly high temperatures and the tackiness so prevalent in such receiving materials is most likely due to its gelation layer.

We have now produced a receiving material suitable for use in the diffusion-transfer copying system which is an improvement over present commercial products and the provision of such a receiving material constitutes the subject of this invention.

According to this invention, a plastic foil base such as that from cellulose acetate, polystyrene, or the like, is coated with a solution comprising organic solvents together with a co-polymer of maleic anhydride and an alkyl vinyl ether, a normally hydrophobic polymer such as cellulose acetate, vinyl acetate, or the like, a silver halide developing agent such as hydroquinone or *p*-aminophenol, a silver halide complexing agent such as 2-hydroxyethylallylthiourea, a water soluble silver salt such as silver nitrate, silver acetate, silver citrate, or the like, which, quite likely, aid in

the nucleation needed to form dense images. Advantageously, traces of an acid corresponding to the anion of the H₂O soluble silver salt are included in our coating solution such as nitric, acetic, citric acids, or the like. The function of the acid is to prevent the silver ion from being reduced by the developing agent before the coated foil has been dried.

The polymer mixture used in coating the foil base is normally hydrophobic and, as such, will not be evenly wet with the aqueous developing solution used in processing. However, such hydrophobic coatings, when treated with certain hydrolytic agents, i.e., a moist nitrogen containing base, are transformed into hydrophilic films. After the coating containing the co-polymer of the alkyl vinyl ether and maleic anhydride has been rendered hydrophilic, the foil coating readily accepts the developer compositions used after exposure. The surface hydrolysis of the alkyl vinyl ether-maleic anhydride co-polymer coating with a water soluble nitrogenous base also neutralizes any mineral acid present in the coating and allows the formation of minute silver grains required in nucleation.

In order to reduce a tendency to curl and to prevent chemical spotting on the back, the foil base coated as above may also be coated on the back side with a solvent solution containing the alkyl vinyl ether-maleic anhydride co-polymer and the hydrophobic polymer.

The alkyl vinyl ether-maleic anhydride co-polymers contemplated for use are for example those described in U.S. P. 2,772,972 and may include those from maleic anhydride, on the one hand, and methyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, 2-methoxyethyl vinyl ether, and the like, on the other hand.

In lieu of the cellulose acetate as the hydrophobic material employed with the maleic anhydride co-polymer, use may be made of the materials such as cellulose propionate, cellulose butyrate, mixed esters such as cellulose acetate propionate, cellulose acetate butyrate, polyvinyl acetates such as polyvinyl butyral, polymethyl acrylate, polymethylmethacrylate, and the like.

As the silver halide complexing agent there may be employed for example N - allyl - 4 - morpholinethiocarbamate, 1 - allyl - 3 - ethyl - 2 - thiourea, 1 - benzyl - 3 - β - hydroxy - ethyl - 2 - thiourea, and the like.

The new transfer foil of this invention produces, in a surprisingly short time, high contrast positive copies of originals with haze-free backgrounds free from yellow discoloration. After processing, the moist foil is completely tack free and dries in a few seconds to a copy very suitable for use in producing further reproductions by, for instance, the diazotype copying process or for use as a master for producing printing plates in a photo-mechanical reproduction process.

The use of the moist organic solvent system from which the transfer material of this invention is coated materially speeds up coating operations with a subsequent saving in cost.

In addition to the above new features and advantages, the new receiving material of this invention possesses the properties and uses of the receiving material of the prior art. Thus, the photographic images formed on our receiving material may be given any of the subsequent treatments employed in photography such as intensification, reduction, toning, colour development, build up of colour images by silver bleaching, and the like.

The present invention is further described by the following examples although it is to be understood that this invention is not limited thereto:

EXAMPLE I

Solution A is made by dissolving 50 g. of polyvinyl methyl ether-maleic anhydride (PVM/MA) with a specific viscosity in 2-butanone at 20° C. of 1.0—1.5, manufactured and sold by General Aniline & Film Corporation, and 25 g. of low viscosity cellulose acetate containing 56% combined acetic acid in a mixture of acetone (3000 ml.) and methyl Cellosolve acetate (250 ml.). "Cellosolve" is a registered Trade Mark.

Solution B contains methanol (1750 ml.), nitric acid (1.75 ml.), hydroquinone (5.0 g.) and 2 - hydroxyethylallylthiourea (2.5 g.). To this is added silver nitrate (2.5 g.) dissolved in 5.0 ml. of water.

Solution B is added to Solution A and the resulting mixture is applied by reverse roll head coating to give a concentration of about 5 ml. per sq. ft. to a cellulose triacetate film base.

After drying, the foil is overcoated with a solution of monoethanolamine (10% in water) using the reverse roll head method at a rate of 5.5 feet per minute and kept wet for about 1 minute before entering a drying chamber. The back side of the foil is now coated by reverse roll head with a solution formulated as Solution A but containing methanol (1750 ml.) in addition. This too is overcoated with 10% monoethanolamine as described above.

A piece of silver halide negative paper is exposed reflex-wise using an opaque original. The exposure is made in a light box such as that manufactured by F. C. Ludwig, Inc., Old Saybrook, Connecticut, and sold under "Contoura." "Contoura" is a registered Trade Mark. After exposure, the negative paper and receiving foil described above are passed through a developing device of the type manufactured by the aforesaid C. F. Ludwig, Inc. and sold under "Constat." "Constat" is a registered Trade Mark. In the developing device, the exposed negative and receiving foil are pressed face to face in the presence of a developer solution containing a silver halide

developing agent and a fixer such as hypo. A few seconds after emerging from the developing device, image transfer from the negative to the receiving material is complete and the two sheets are peeled apart. The receiving foil, only slightly damp, contains a completely clear black and white positive of the opaque original.

A developing composition suitable for use in the above developing device is as follows:

Hydroquinone	13.0 g.
Sodium sulphite	40.9 g.
Sodium thiosulphate	21.5 g.
Potassium bromide	2.5 g.
Phenidone	1.0 g.
Sodium hydroxide	10.0 g.
Water	26 ounces

"Phenidone" is a registered Trade Mark.

EXAMPLE II

A receiving foil was prepared according to Example I except that the low viscosity cellulose acetate used therein for solution A was replaced by a vinyl acetate resin. The particular vinyl acetate employed had an intrinsic viscosity in cyclohexanone of 0.11 at 20° C. and is manufactured and sold as grade AYAC by the Bakelite Corporation, 30 East 42nd Street, New York, N.Y.

After exposing and processing as in Example I, excellent clear back and white positive images of the opaque copy material were obtained.

EXAMPLE III

The same procedure was carried out as in Example I except that 50.0 g. of poly-2-chloroethyl vinyl ether-maleic anhydride was used in place of the PVM/MA.

EXAMPLE IV

Using polyethyl vinyl ether-maleic anhydride in lieu of PVM/MA, the procedure in this example was carried out as given in Example I.

EXAMPLE V

The procedure was the same as in Example I excepting that 25.0 g. of a vinyl acetate resin having an intrinsic viscosity in cyclohexanone at 20° C. of 0.11 was used as the hydrophobic resin in lieu of cellulose acetate. The resulting foil, when processed as in Example I, gave results comparable to those obtained in said Example I.

EXAMPLE VI

Using 25.0 g. of a low viscosity, low hydroxy polyvinyl butyral having a viscosity of 23 cps. (5% in ethanol) in lieu of the cellulose acetate, a cellulose acetate receiving foil was prepared, exposed and developed as in Example I. A clear black and white positive image of the opaque copy material was obtained.

EXAMPLE VII

The procedure of Example I was carried out using polybutyl vinyl ether-maleic anhydride in lieu of PVM/MA. The results were comparable to those obtained in Example I.

EXAMPLE VIII

The procedure of Example I was carried out using polyvinyl isobutyl ether-maleic anhydride in lieu of PVM/MA. The results were comparable to those obtained in Example I.

EXAMPLE IX

The procedure of Example I was carried out using poly-2-methoxyethyl vinyl ether-maleic anhydride in lieu of PVM/MA. The results were comparable to those obtained in Example I.

WHAT WE CLAIM IS:—

1. A receiving material for use in the photographic diffusion-transfer process comprising a support and a layer on said support comprising a polyalkyl vinyl ether-maleic anhydride co-polymer, a hydrophobic resin or cellulose derivative compatible therewith, a silver halide developing agent, a silver halide complexing agent, and a water soluble silver salt, said layer being rendered water receptive by treatment with an alkali.

2. The product as defined in claim 1, wherein the alkali is a moist water soluble nitrogenous base.

3. The product as defined in claim 1 or claim 2, wherein the support is a transparent plastic.

4. The product as defined in claim 3, wherein the support is a cellulose triacetate.

5. The product as defined in any preceding claim, wherein the polyalkyl vinyl ether-maleic anhydride co-polymer is polyvinyl methyl ether-maleic anhydride co-polymer.

6. The product as defined in any preceding claim, wherein the cellulose derivative is cellulose acetate.

7. The product as defined in any preceding claim, wherein the water soluble silver salt is silver nitrate.

8. The product as defined in any claim, wherein the silver complexing agent is a thiourea derivative, one nitrogen atom of which is joined through a methylene group to a grouping of carbon atoms containing a $>C=C<$ radical directly linked to said methylene group, and the other nitrogen atom of which is strongly basic by virtue of a chemical structure selected from the class consisting of those in which the nitrogen atom is substituted by an aliphatic radical and those in which the nitrogen atom forms part of a saturated heterocyclic ring.

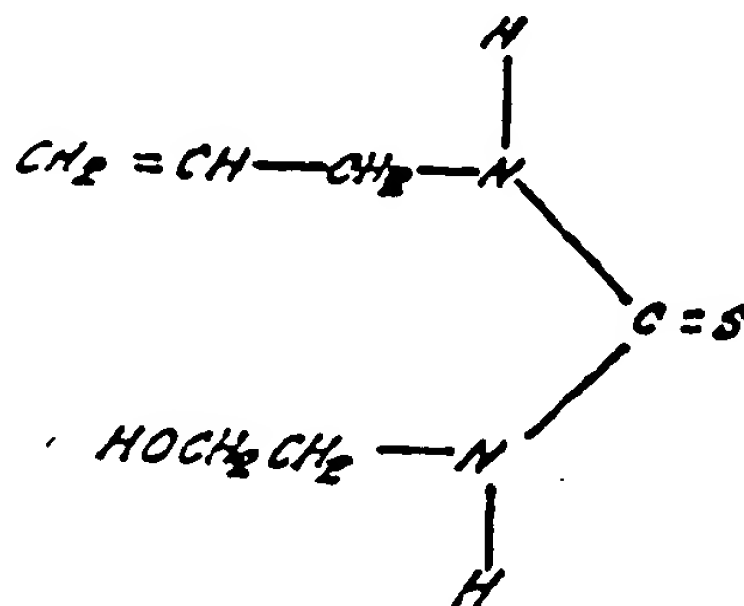
9. The process of producing a material for use in the photographic diffusion transfer process which comprises coating a support with a polyvinyl alkyl ether-maleic anhydride co-polymer, a hydrophobic resin or cellulose derivative compatible therewith, a silver halide developing agent, a silver halide complexing agent, and a water soluble silver salt, and rendering said coating water receptive by treating with an alkali.

10. In the process of producing a material

5 for use in the photographic diffusion transfer process which comprises coating a support with a polyvinyl alkyl ether-maleic anhydride copolymer, a hydrophobic resin or cellulose derivative compatible therewith, a silver halide developing agent, a silver halide complexing agent, and a water soluble silver salt, the improvement of which comprises adding to

the coating, an acid, the anion of which is identical with the anion of said water soluble silver salt, said layer being rendered water receptive by treatment with an alkali. 10

11. The product as defined in claim 8 wherein the thiourea derivative has the following formula: 15



12. A product according to claim 1 substantially as herein described and exemplified.

20 13. A process according to claim 9 substantially as herein described and exemplified.

MEWBURN, ELLIS & CO.,
70 & 72, Chancery Lane, London, W.C.2.
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press, 1960.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.